

Novel Nanocomposite Membrane Structures for Hydrogen Separations

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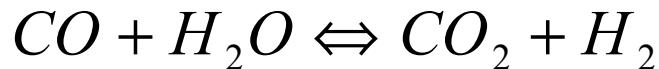
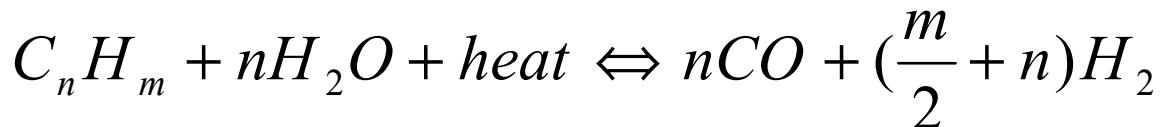
2003 DOE University Coal Research Contractors' Meeting

Pittsburgh, Pennsylvania

May 2003

Synthesis Gas Production

- >90% of world's H₂ is produced via hydrocarbon steam reforming.



- Carbon sources (e.g., coal) contain impurities (e.g., H₂S, COS, SO₂) that appear in syngas product.
- Membranes for syngas purification should be more permeable to contaminants (e.g., H₂S, CO₂) than to H₂ to produce high pressure, high purity syngas product.

Gas Separation Using Membranes

Current applications:

- Air separation - mainly N₂ enriched air
- Natural gas treatment - acid gas removal
- H₂ separation - H₂ from hydrocarbons, ammonia purge, syngas
- Removal of vapors from mixtures with light gases (vapor separation)

Advantages:

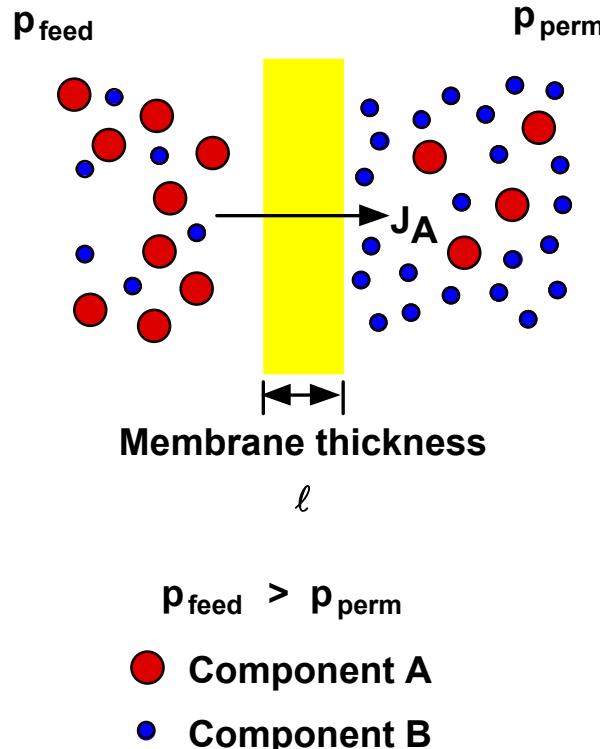
- Low energy separation (no phase change)
- Reliable (no moving parts)
- Small footprint

Drawbacks:

- Incomplete separation (need higher selectivity)
- Low chemical/thermal stability (need more resistant materials)

Gas Transport in Polymers: Solution-Diffusion Mechanism

Upstream pressure



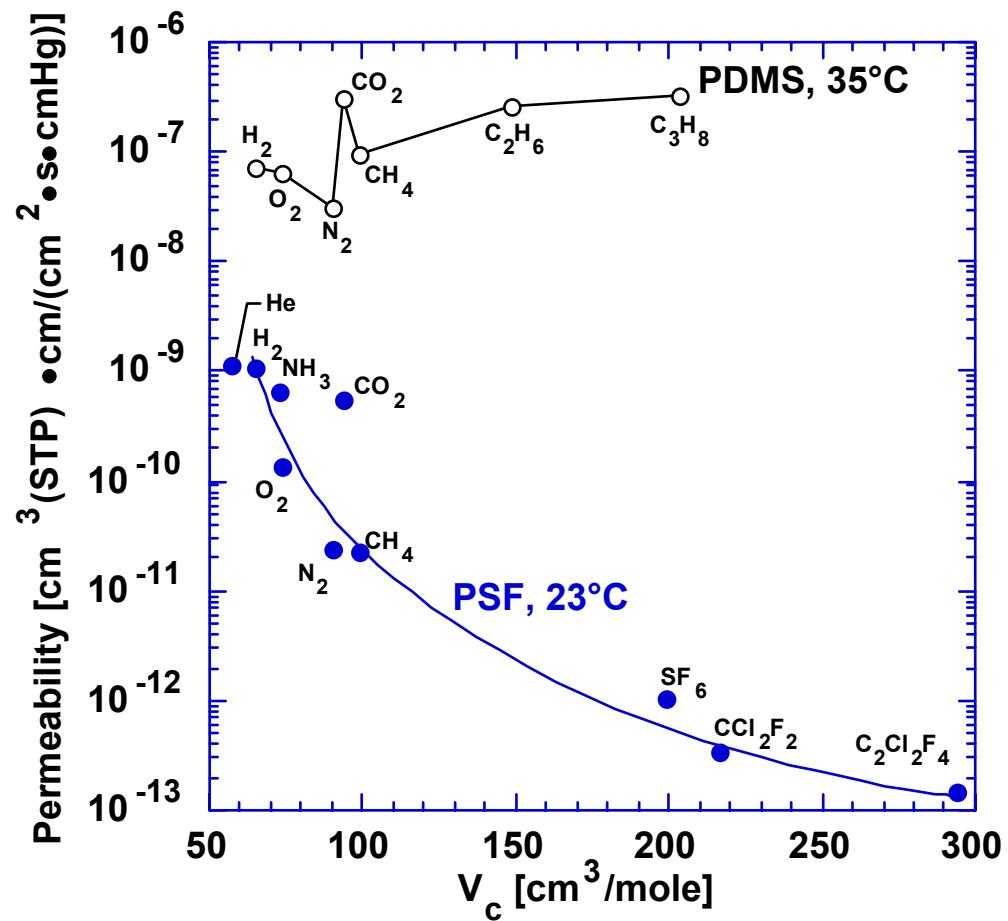
Downstream pressure

- Flux of A $\equiv J_A = \frac{P_A (p_{\text{feed},A} - p_{\text{perm},A})}{\ell}$
- Permeability of A $\equiv P_A = D_A S_A$,
where $D_A \equiv$ Diffusion coefficient of A
 $S_A \equiv$ Solubility coefficient of A
- Selectivity $\equiv \alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right)$

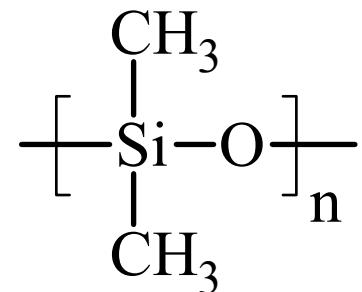
↑
Mobility selectivity ↓
Solubility selectivity

- (1) Sorption on upstream side
- (2) Diffusion down partial pressure gradient
- (3) Desorption on downstream side

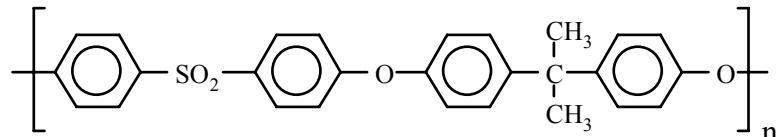
Gas Transport in Polymers: Diffusivity-Selective & Solubility-Selective



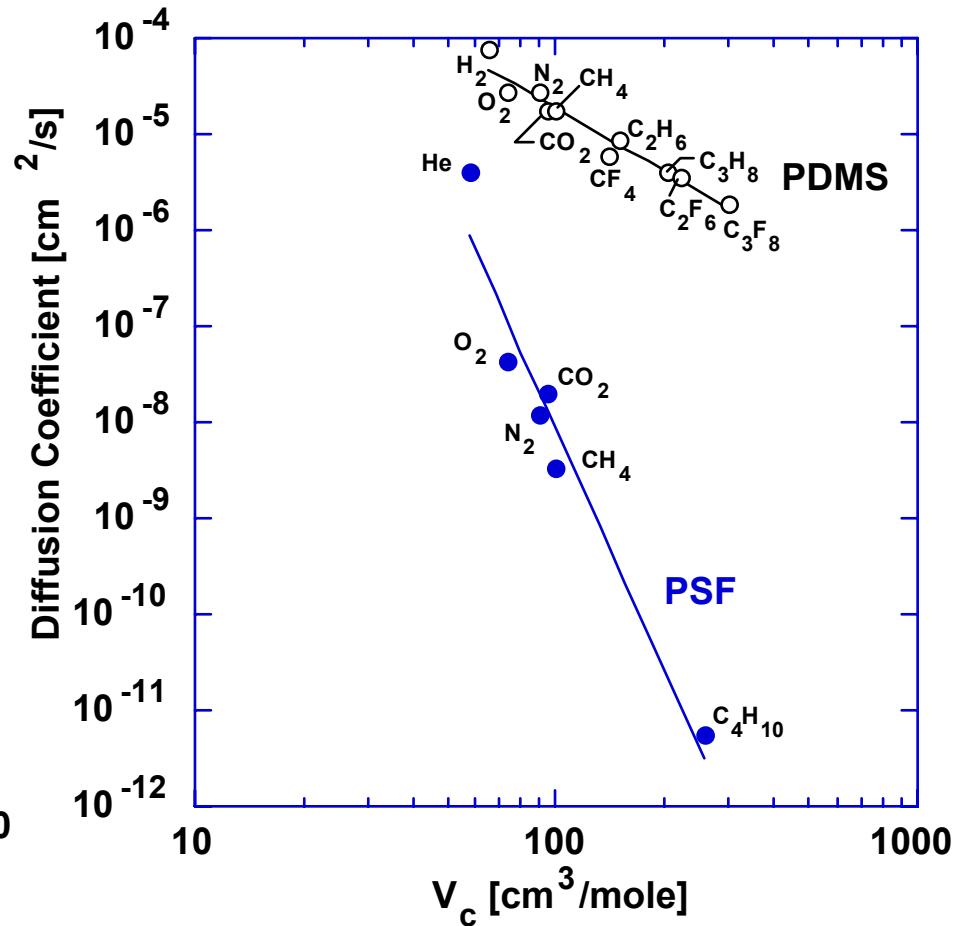
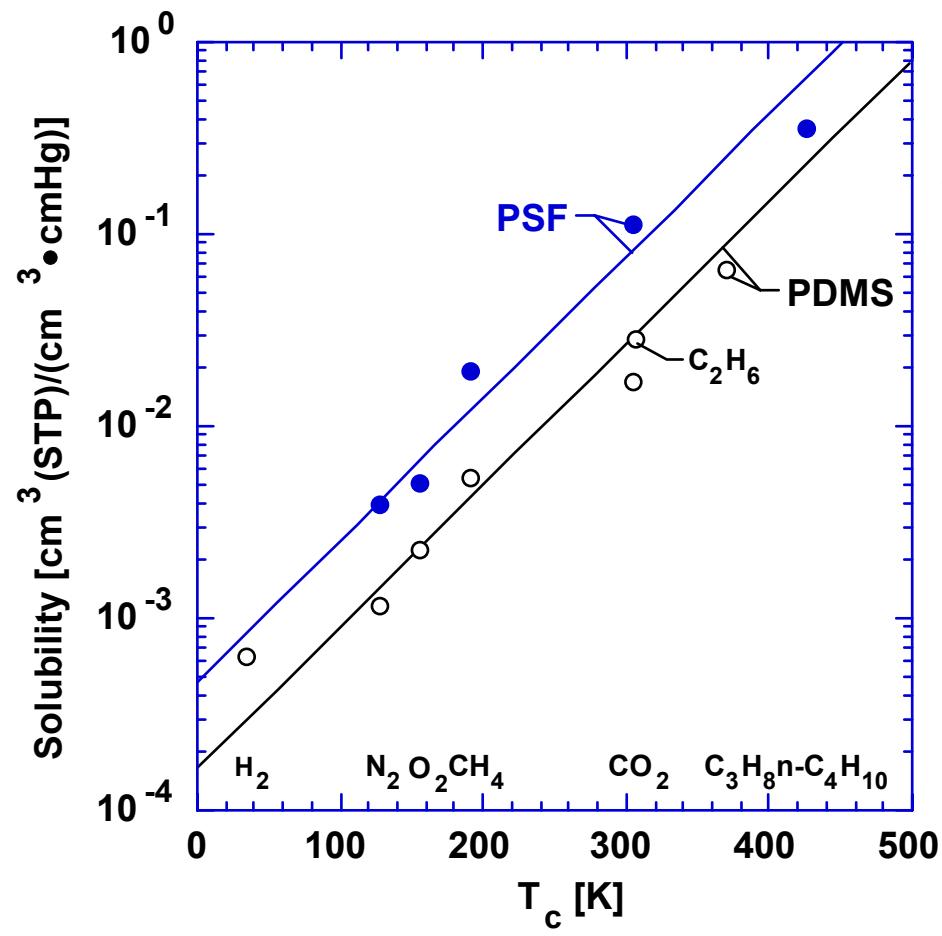
PDMS:



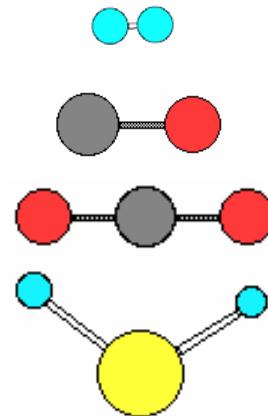
PSF:



Solubility & Diffusivity in Polymers: Diffusivity-Selective & Solubility-Selective Materials



Physical Properties of Key Syngas Components



Penetrant	Size	Condensability
	Critical Volume, cm ³ /mole	Critical Temperature, K
H ₂	65.1	33.2
CO	93.1	132.9
CO ₂	93.9	304.2
H ₂ S	98.6	373.2

CO₂ and H₂S have much higher critical temperatures than H₂ or CO. This difference in critical temperatures makes them ideal candidates for separation using “solubility selective” polymer membranes.

Separation Based on High Solubility Selectivity

$$P = S \times D$$

$$\alpha = \frac{P_{acid\ gas}}{P_{H_2}} = \frac{D_{acid\ gas}}{D_{H_2}} \frac{S_{acid\ gas}}{S_{H_2}}$$

$$\frac{S_{acid\ gas}}{S_{H_2}} \gg 1$$

$$\frac{D_{acid\ gas}}{D_{H_2}} < 1$$

$$\therefore \alpha > 1$$

Optimum Materials Characteristics:

Weak size-sieving ability

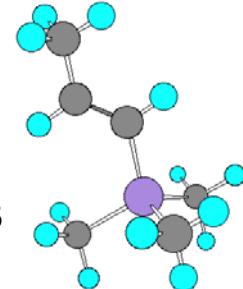
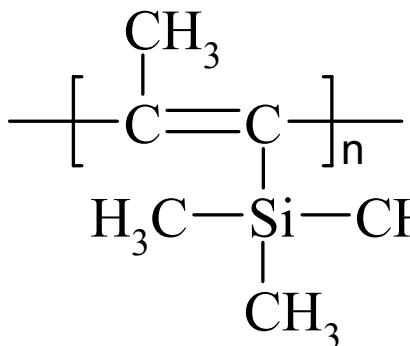
Specific, favorable interactions between acid gas and polymer matrix

Technical Challenge: Most Gas Separation Polymers are H₂ Selective

Type	Polymer	Permeability		Selectivity
		H ₂	CO ₂	CO ₂ /H ₂
Glassy	Polysulfone (PSF)	14.0	5.6	0.40
	Polycarbonate (PC)	14.0	6.5	0.46
	Poly(4-methyl-1-pentene) (PMP)	97.8	83	0.85
	poly(2,6-dimethylphenylene oxide) (PPO)	105	61	0.58
	Cellulose Acetate (CA)	13.6	5.5	0.40
	polyimide formed from 4,4'-hexafluoroisopropylidenediphthalic anhydride and metaphenylenediamine (6FDA-MPD)	50.0	24.2	0.48
Rubbery	cis-polyisoprene(PI)	49	134	2.7

Pure gas permeability coefficients at 35°C. All data (except 6FDA-MPD) are from Zolandz and Fleming (R. R. Zolandz and G. K. Fleming, *Gas Permeation*, in W. S. W. Ho and K. K. Sirkar (Eds.), Membrane Handbook, Van Nostrand Reinhold, New York, p. 17, 1992). 6FDA-MPD data are from Stern (Polymers for gas separations: the next decade, *J. Membrane Sci.*, **94**, p. 1 (1994).). Permeabilities are in Barrers, where 1 Barrer=10⁻¹⁰ cm³(STP) cm/(cm² s cm Hg).

Highly Solubility-Selective Polymers



PTMSP

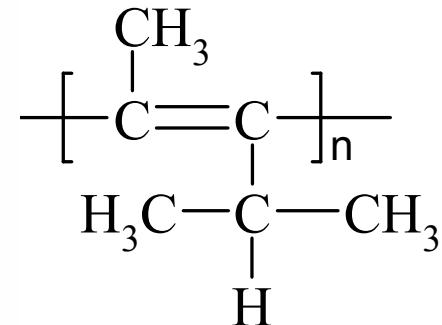
$T_g > 250^\circ\text{C}$

FFV = 0.29

$P_{\text{n-C}_4\text{H}_{10}} = 87,000 \text{ Barrer}$

$\alpha_{\text{n-C}_4\text{H}_{10}/\text{CH}_4} = 47$

Highly soluble



PMP

$T_g > 250^\circ\text{C}$

FFV = 0.28

$P_{\text{n-C}_4\text{H}_{10}} = 5,800 \text{ Barrer}$

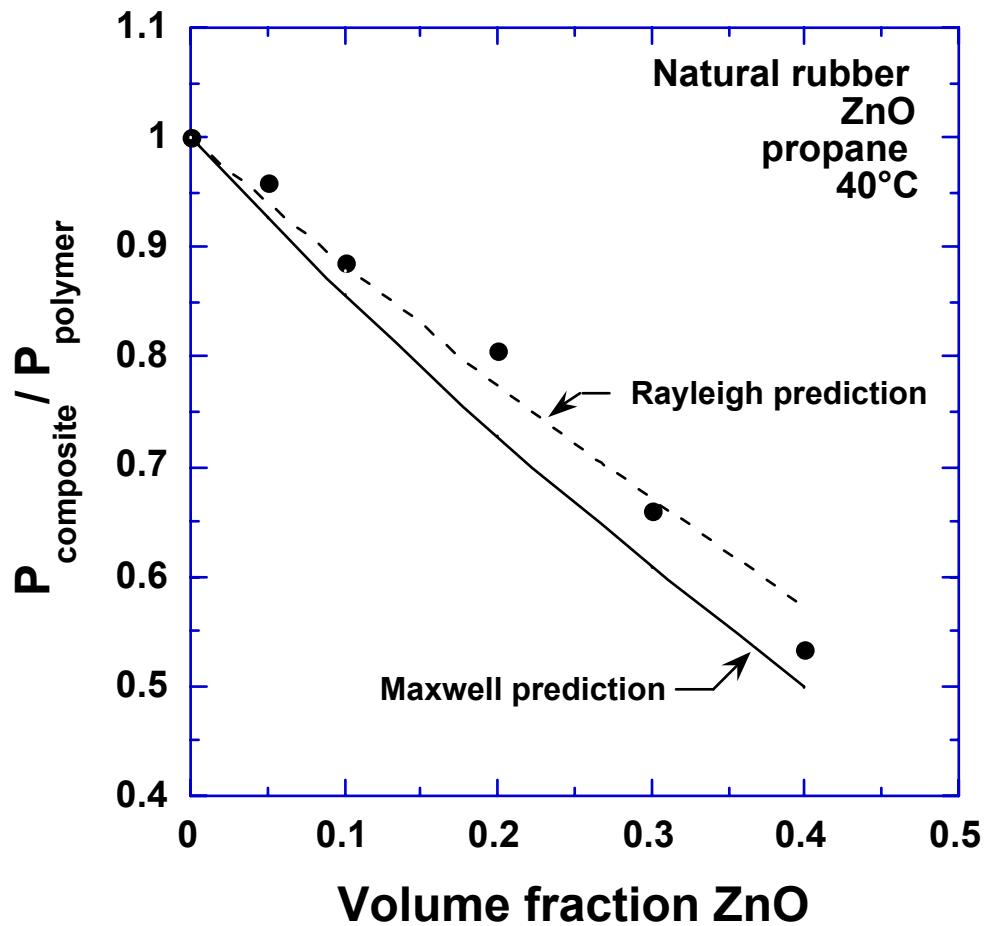
$\alpha_{\text{n-C}_4\text{H}_{10}/\text{CH}_4} = 13.2$

Soluble only in cyclohexane

$$1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s cmHg})$$

Filled Polymer Membranes: Background

Nonporous, impermeable filler



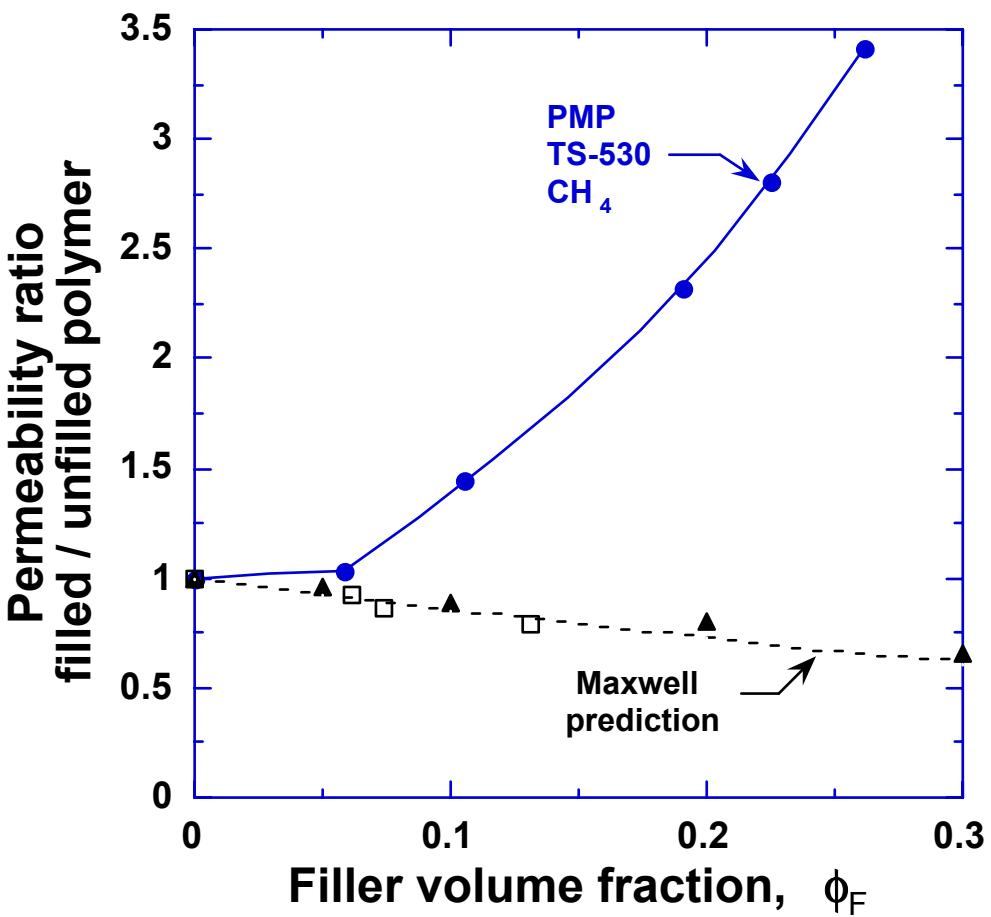
If:

1. Polymer chains wet or interact well with particles and
2. The particles do not change the properties of the polymer,

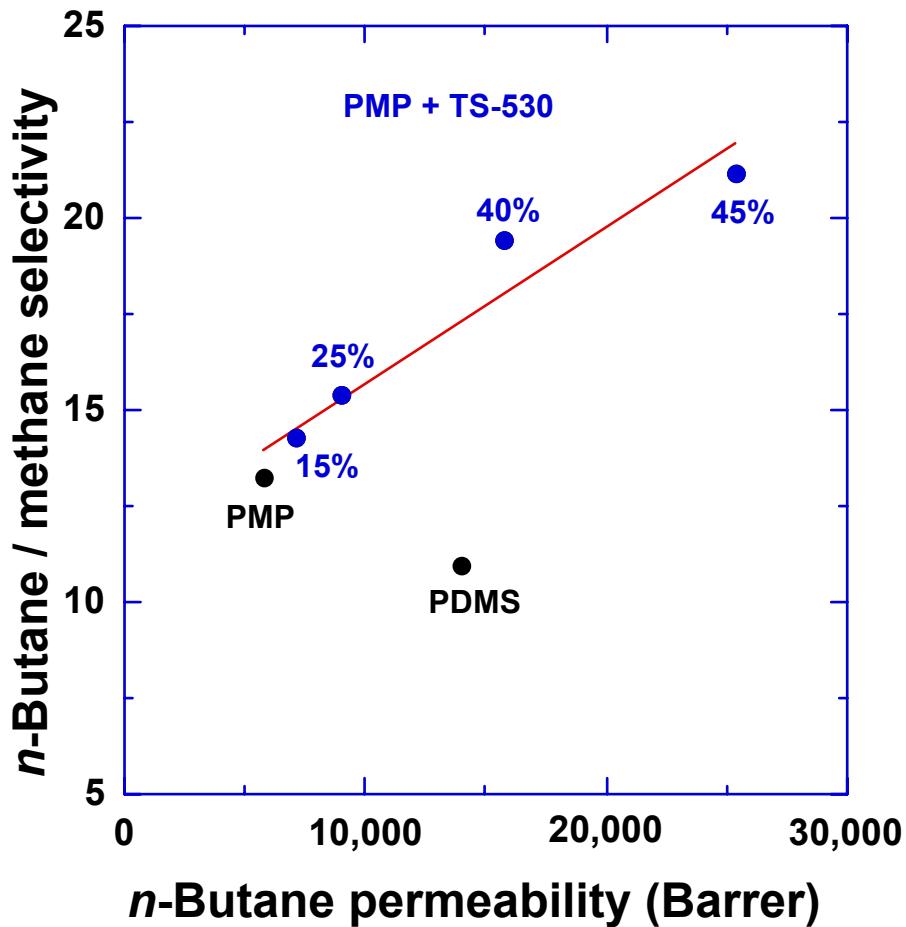
Then addition of nonporous impermeable fillers reduces permeability and has no effect on selectivity.

However, if the above assumptions are not obeyed, the results can be quite different . . .

Effect of Silica Filler on PMP Permeability and Mixed-Gas Selectivity

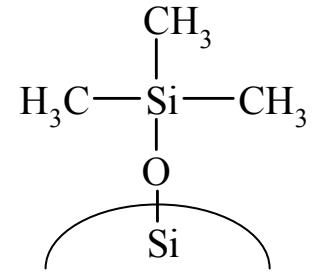
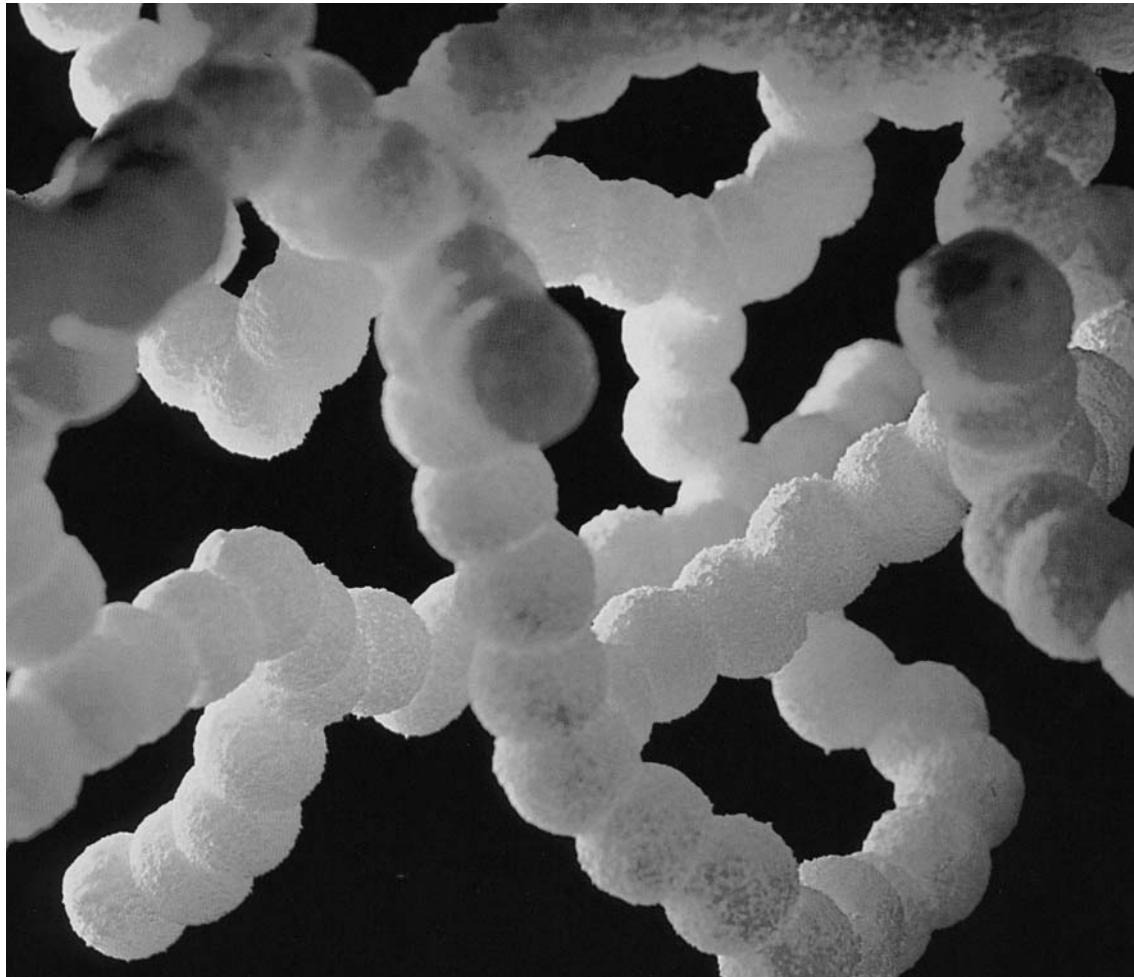


▲ Barrer et al., *Journal of Polymer Science*, **1**, 1963
□ : Most, *Journal of Applied Polymer Science*, **14**, 1970

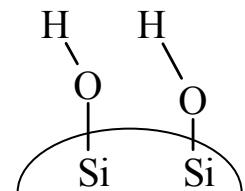


2 % n-butane / 98% methane feed;
upstream pressure = 150 psig; downstream pressure = 0 psig

Chain-like Aggregates of Spherical Fumed Silica Primary Particles

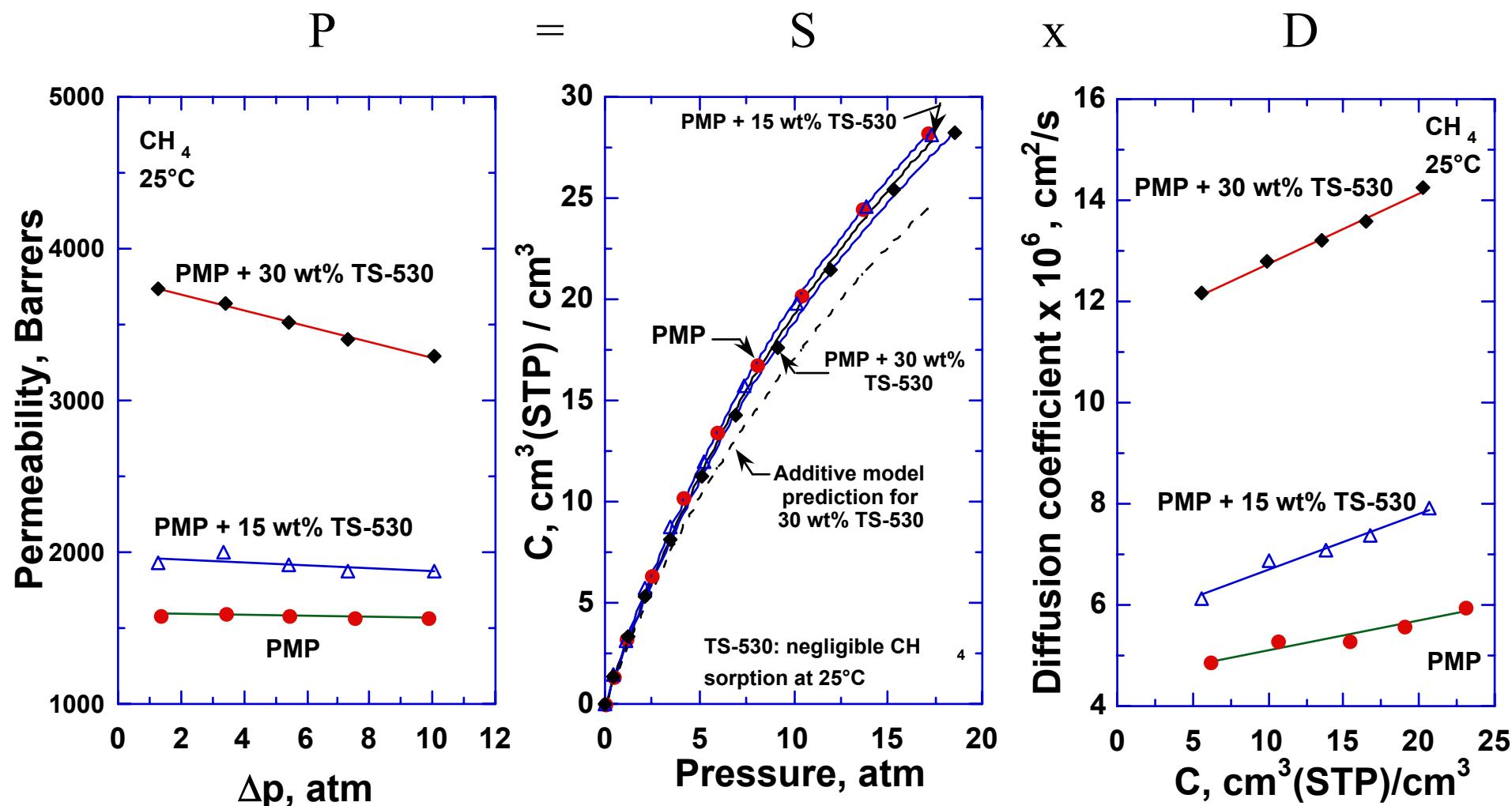


**Surface Treated
Hydrophobic TS-530**



**Untreated
Hydrophilic EH-5**

Methane Permeability, Solubility, and Diffusivity in TS-530 Filled PMP



$15 \text{ wt\%} = 6 \text{ vol\%}, 30 \text{ wt\%} = 13 \text{ vol\%}$

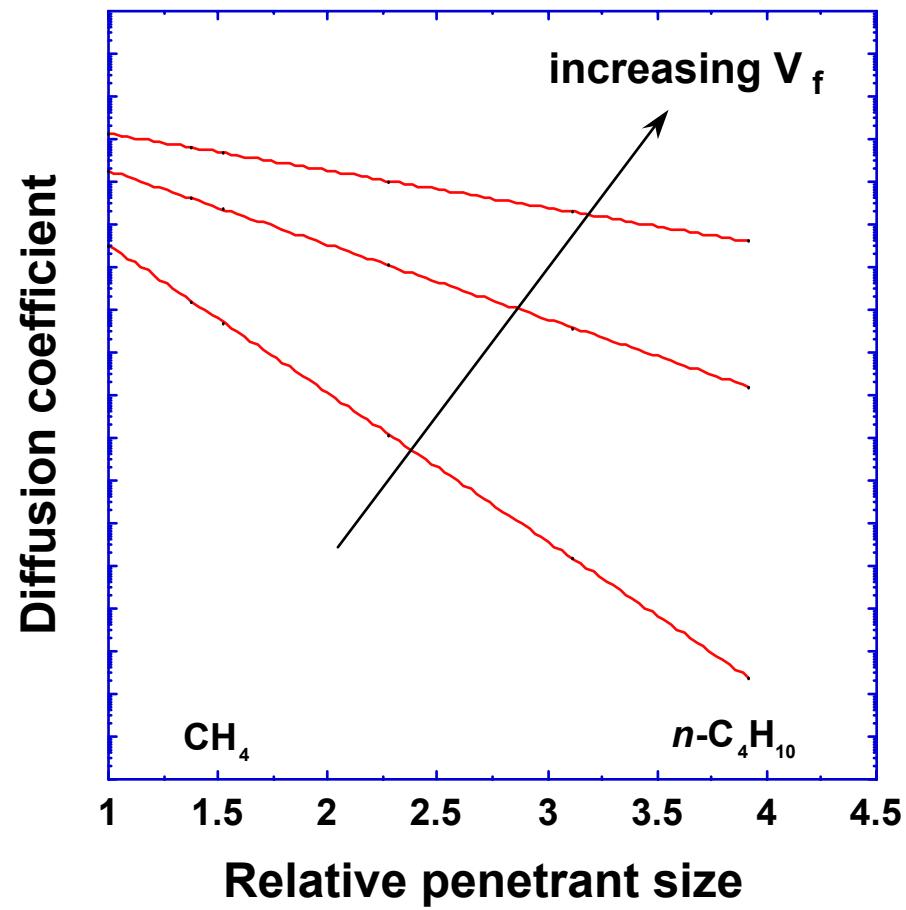
T.C. Merkel et al., *Chemistry of Materials*, 15, 109-123 (2003).

Effect of Free Volume on Diffusion Coefficients

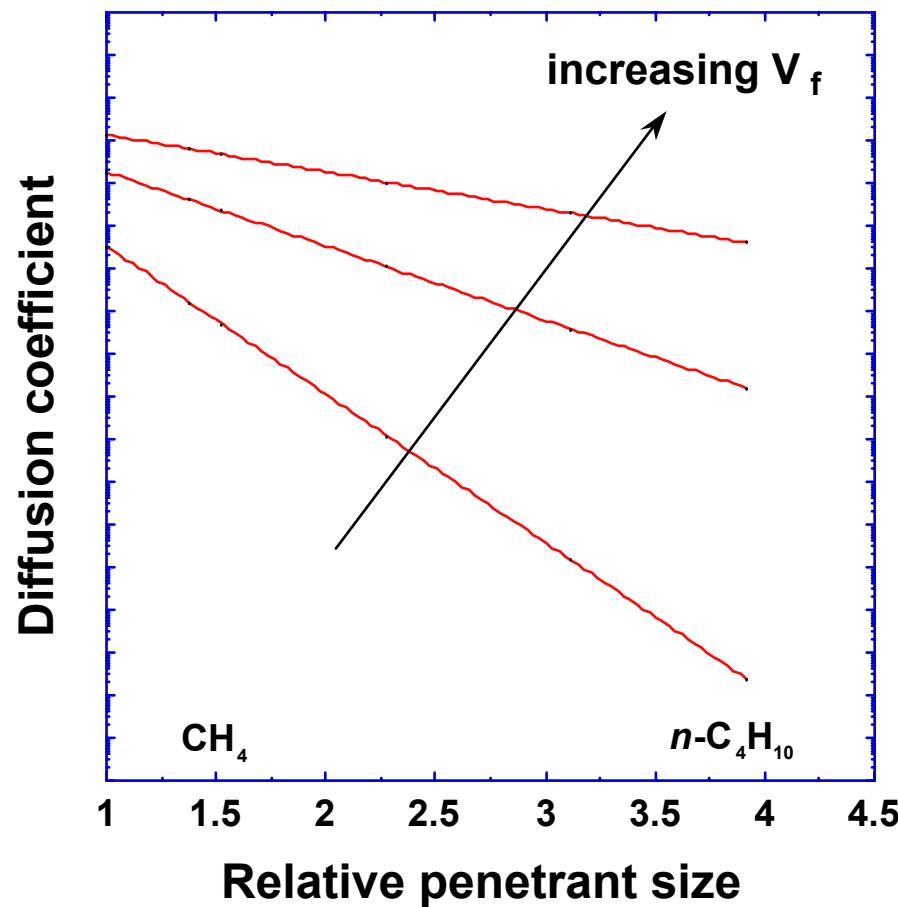
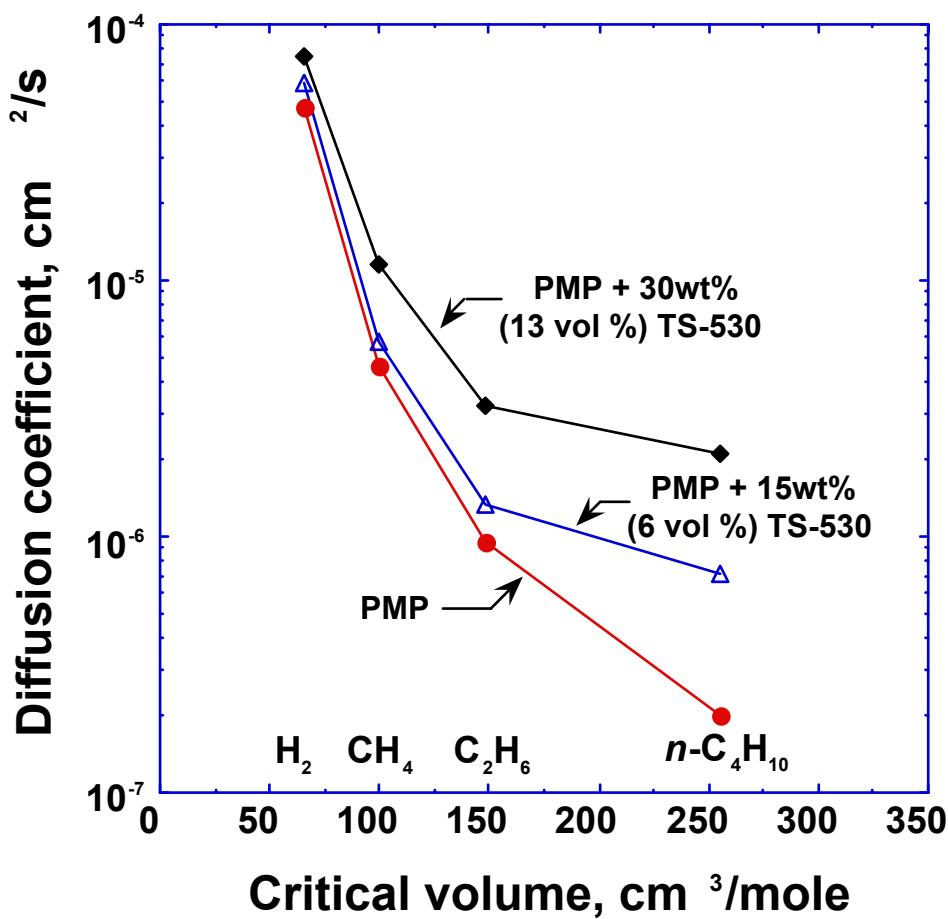
Minimum free volume
size accessible to penetrant

$$D = A \exp \left[-\frac{\gamma V^*}{V_f} \right]$$

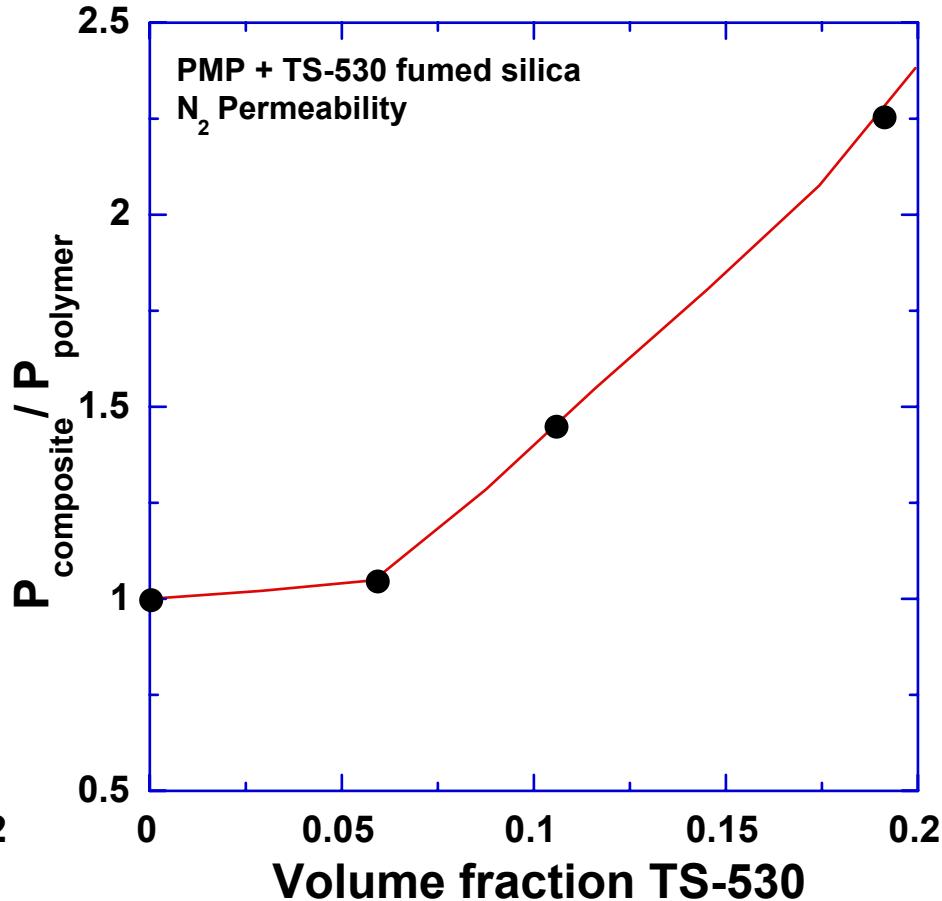
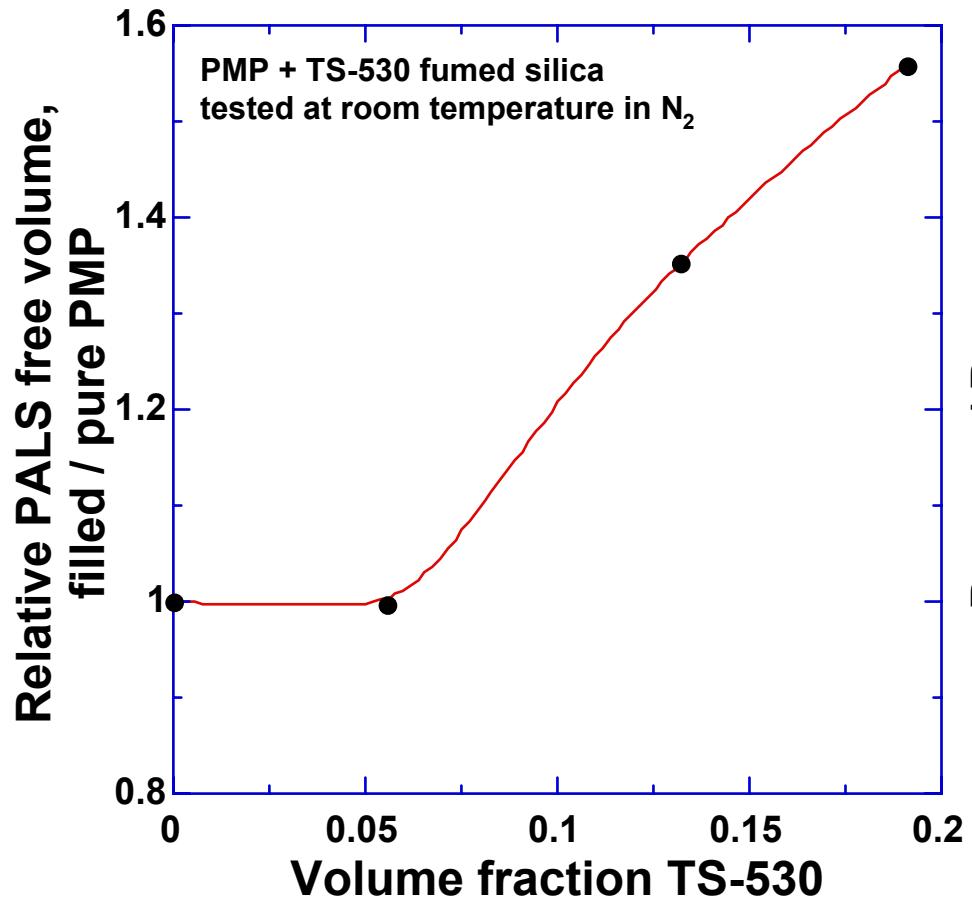
Average polymer
free volume



Effect of TS-530 on Diffusion Coefficients in PMP

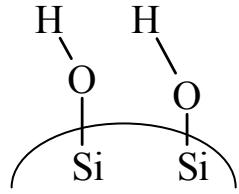
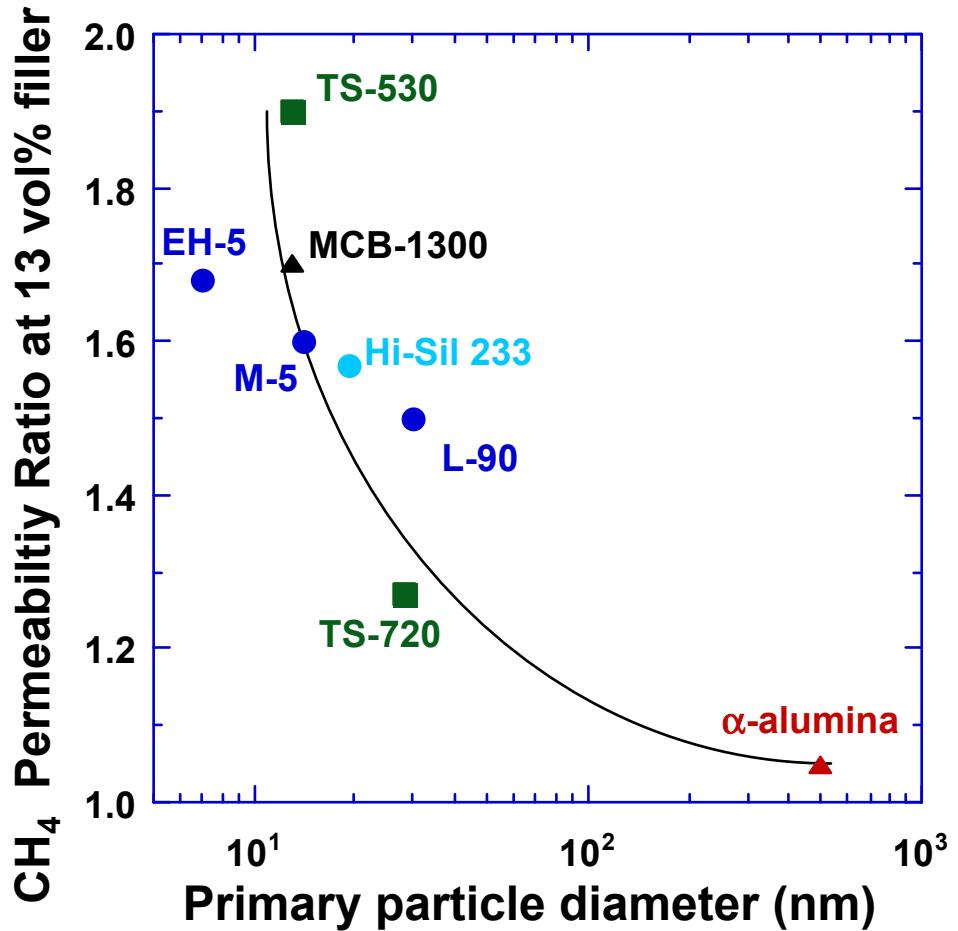


Filled PMP: Comparison of PALS Free Volume with Nitrogen Permeability

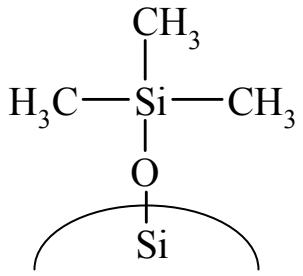


PALS data were obtained through a collaboration with Dr. Anita J. Hill, CSIRO, Melbourne, Australia

Effect of Filler Primary Particle Size on Permeability Enhancement

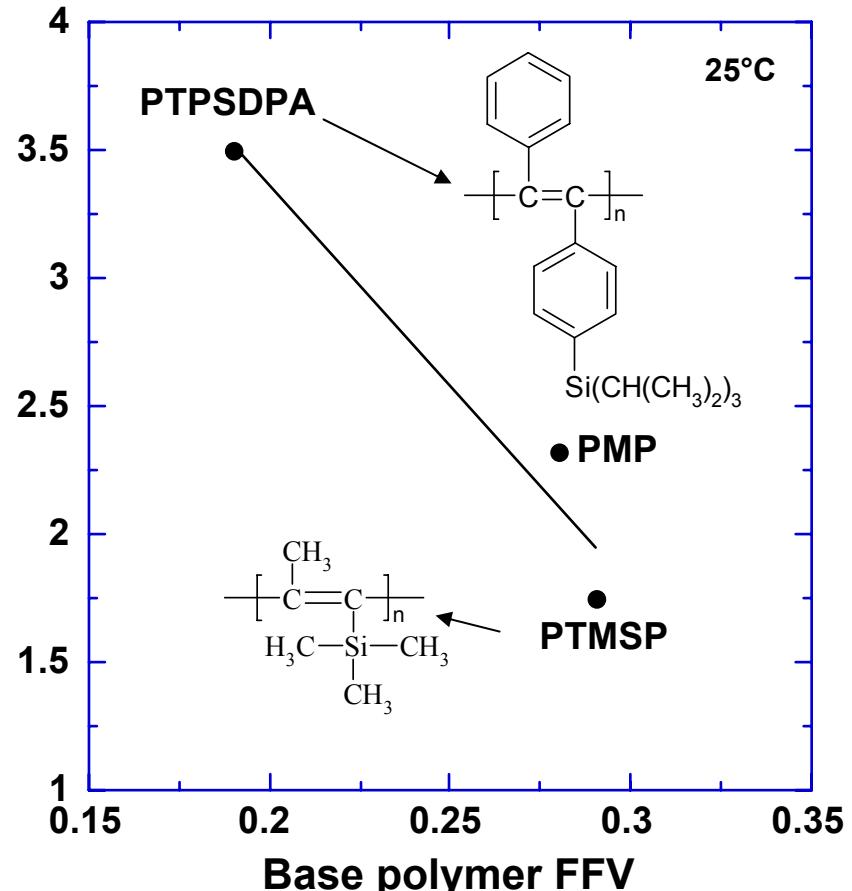
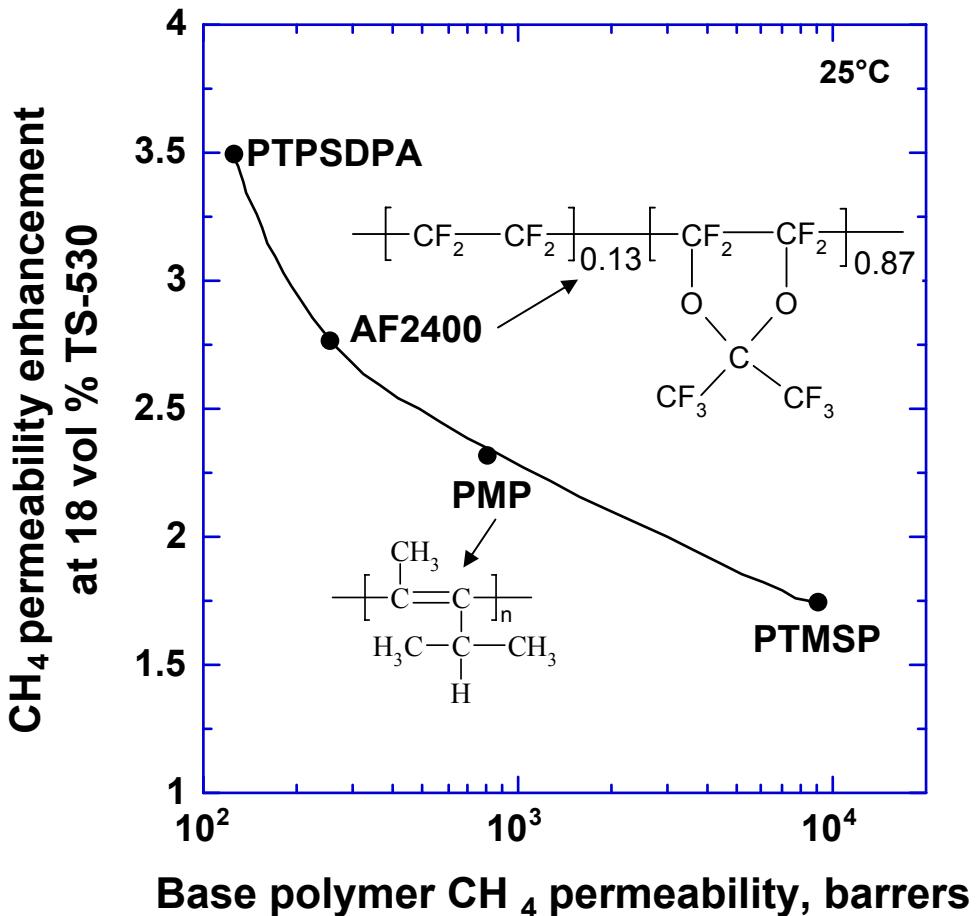


Hydrophilic
(L-90, M-5, EH-5)



Hydrophobic
TS-530, TS-720

Effect of Polymer Free Volume on Permeability Enhancement



CO_2/H_2 Separation

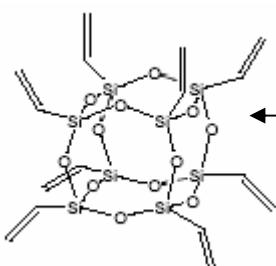
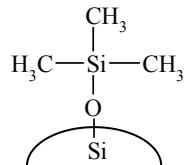
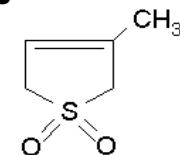
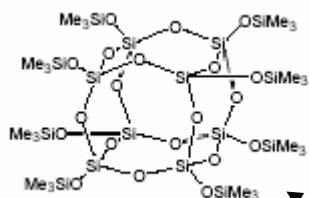
Polymers and Fillers Considered

Polymers

- (i) PTMSP = Poly(1-trimethylsilyl-1-propyne)
[High-free-volume, glassy polyacetylene]
- (ii) PEBA^X = Polyether-polyamide block copolymer

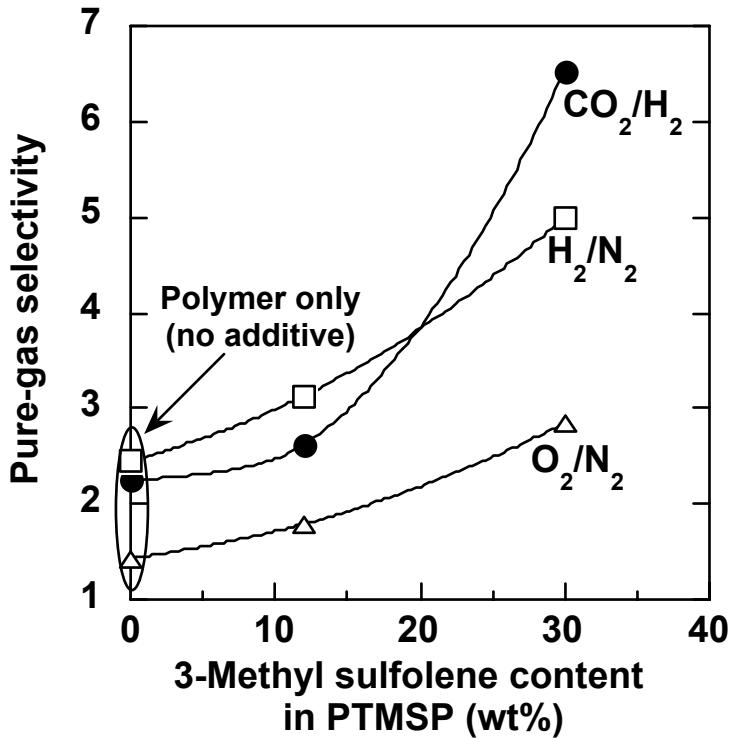
Fillers

- (i) 3-methyl sulfolene ($\text{C}_5\text{H}_8\text{SO}_2$)
---> Acid-gas adsorbent with sulfone groups
- (ii) Cab-O-Sil[®] TS-530
---> Hydrophobic, trimethylsilylated fumed silica
- (iii) POSS MS0865 nanoparticles*
---> Octatrimethylsiloxy-POSS ($\text{C}_{24}\text{H}_{72}\text{O}_{20}\text{Si}_{16}$)
- (iv) POSS OL1160 nanoparticles*
---> Octavinyl-POSS ($\text{C}_{16}\text{H}_{24}\text{O}_{12}\text{Si}_8$)



* POSS = Polyhedral oligomeric silsesquioxanes
(Single-molecule Si-O cage structures with peripheral organic groups
that can be systematically varied and functionalized)

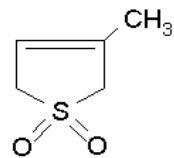
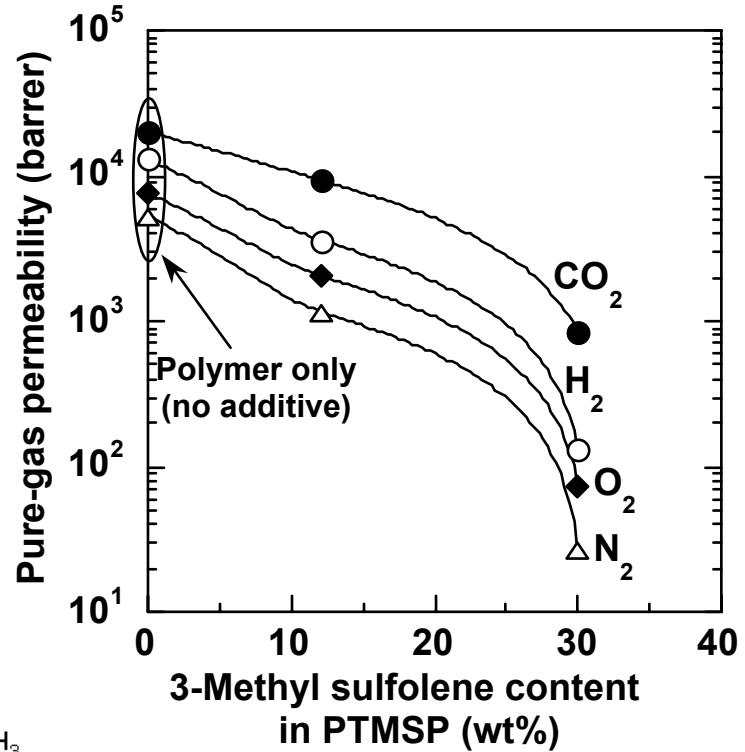
Addition of 3-Methyl Sulfolene Adsorbent to Intrinsically Low-Selectivity PTMSP: Selectivity Improvement



Feed pressure = 50 psig

Permeate pressure = 0 psig

T = 21 °C



1 barrer = $10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$

Addition of 3-Methyl Sulfolene Adsorbent to Intrinsically High-Selectivity PEBA^X: No Selectivity Improvement

3-Methyl sulfolene content in PEBA ^X 1074 (wt%)	Pure-gas permeability (barrer)		CO ₂ /H ₂ selectivity	
	H ₂	CO ₂	Pure-gas	Mixed-gas
0 (Unfilled PEBA ^X 1074)	6.8	57	8.4	8.4
10	6.8	62	9.1	8.0
30	7.3	62	8.5	ND

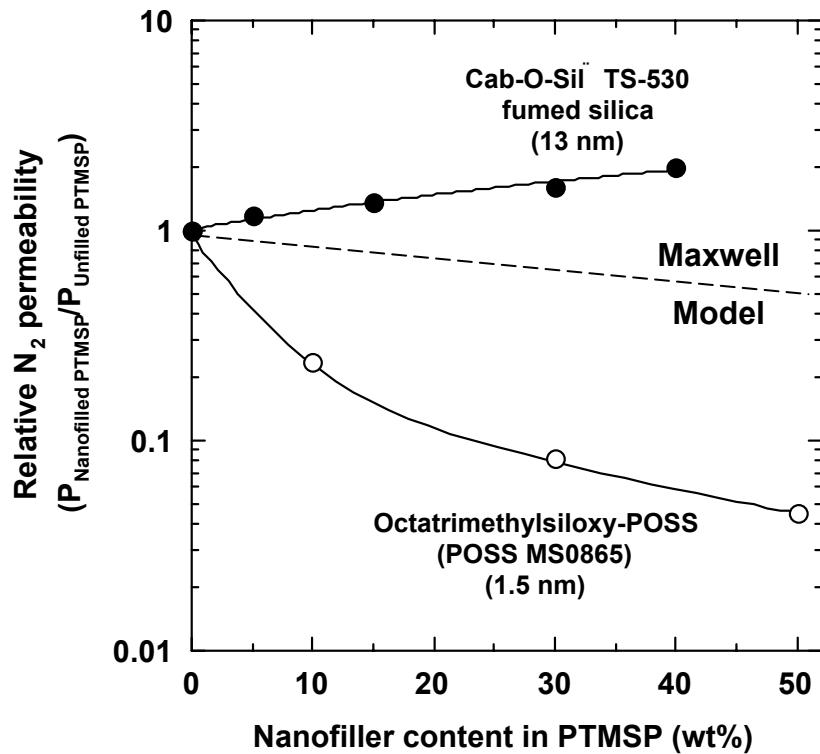
1 barrer = 10⁻¹⁰ cm³(STP)·cm/(cm²·s·cmHg)

ND = Not determined

Pure-gas test conditions: Feed pressure = 50 psig; Permeate pressure = 0 psig;
He sweep used; T = 21 °C

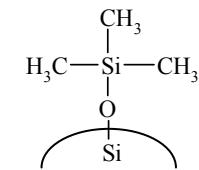
Mixed-gas test conditions: Binary 25.2% CO₂/74.8% H₂ feed
Feed pressure = 50 psig; Permeate pressure = 0 psig; He sweep used;
Stage-cut < 1%; T = 21 °C

Nitrogen Permeability Behavior in PTMSP Filled with Two Different Nanoparticle Fillers: Effect of Filler Content

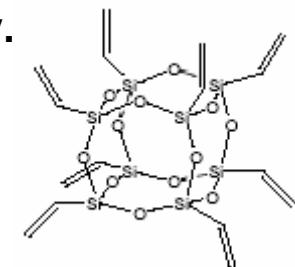


Fumed silica and POSS fillers have surprisingly opposite effect on gas permeability in PTMSP.

- TS-530 fumed silica nanoparticles increase permeability.



- POSS nanoparticles dramatically decrease permeability.



Feed pressure = 50 psig; Permeate pressure = 0 psig; T = 23 °C

Nitrogen Permeability in PTMSP Containing POSS and/or Fumed Silica Nanoparticles

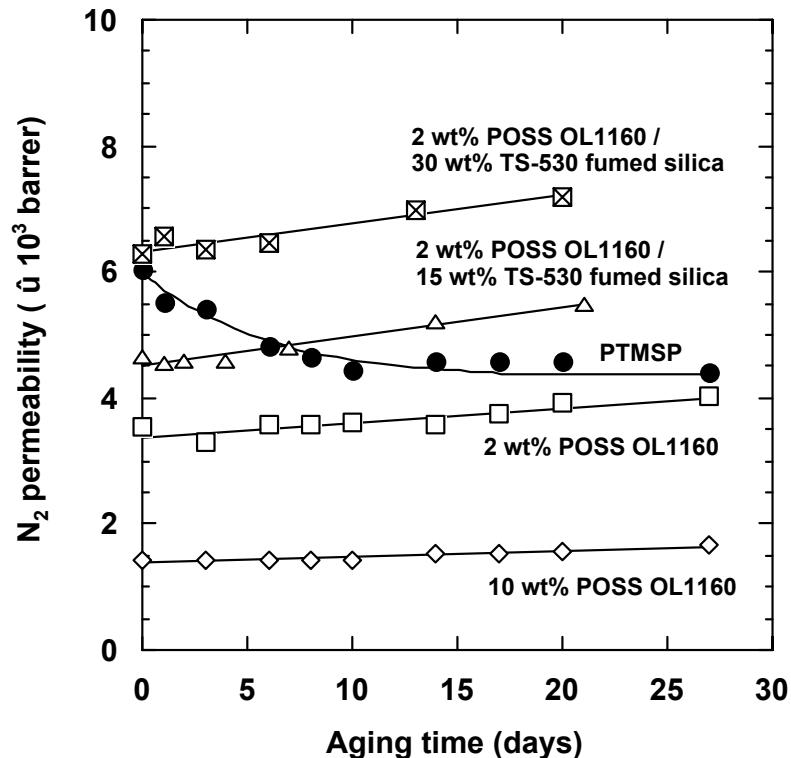
Nanofiller content in PTMSP (wt%)		N_2 permeability (barrer)	N_2 permeability <u>relative to</u> pure PTMSP (unfilled)
POSS OL1160	TS-530 fumed silica		
0	0	6,000	1.0
2	0	3,500	0.58
2	15	4,600	0.77
0	30	8,500	1.4
2	30	6,300	1.1

1 barrer = 10^{-10} cm³(STP)·cm/(cm²·s·cmHg)

Feed pressure = 50 psig; Permeate pressure = 0 psig; T = 23 °C

---> Permeability of binary fumed silica/POSS filler system appears to be an average of permeabilities in the respective single-filler systems.

Nitrogen Permeability in PTMSP and PTMSP Containing Various Nanofillers: Effect of Aging Time

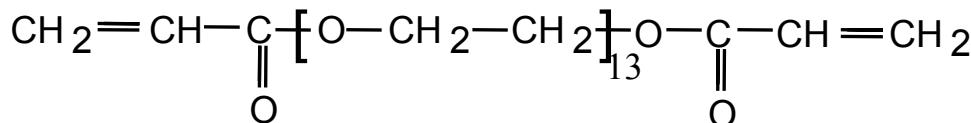


- Pure PTMSP is notorious for marked physical aging at ambient conditions, leading to a reduction in permeability over time.
- Addition of POSS nanoparticles appear to arrest aging in PTMSP and stabilize permeability in PTMSP.
- Incorporation of both POSS and fumed silica particles lead to both higher permeability (presumably due to the silica) and resistance to aging and permeability decline (due to POSS).

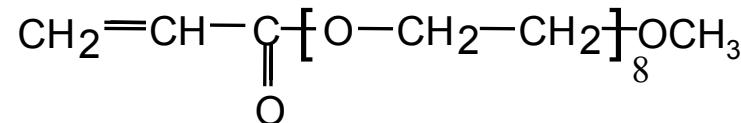
$$1 \text{ barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$$

Feed pressure = 50 psig; Permeate pressure = 0 psig; T = 23 °C

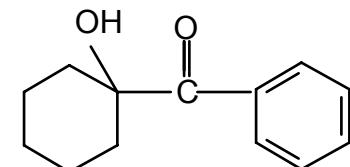
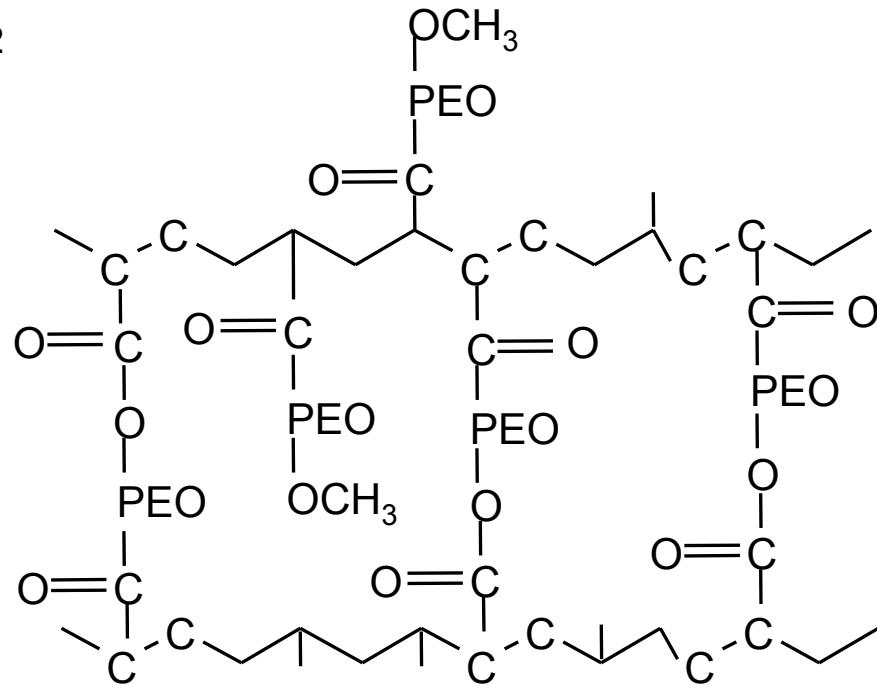
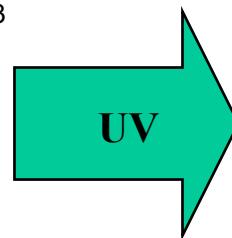
Crosslinked Poly(ethylene oxide) [XLPEO]



Poly(ethylene oxide) diacrylate (MW=700)



Poly(ethylene oxide) acrylate (MW=454)



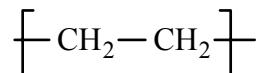
Initiator: 1-Hydroxycyclohexyl phenyl ketone (0.1 wt.%)

Chemical Structure of XLPEO

Chemical Structures

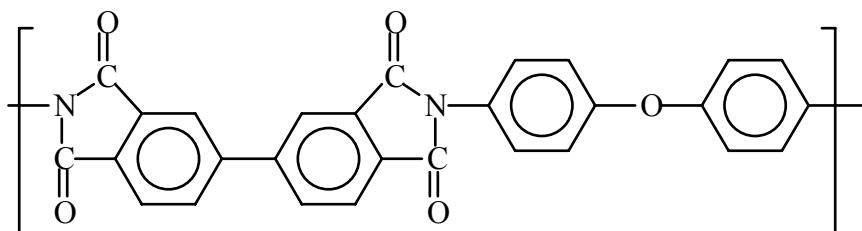
PE = poly(ethylene)

(Michaels & Bixler, *J. Polym. Sci.*, **50**, 413, 1961)



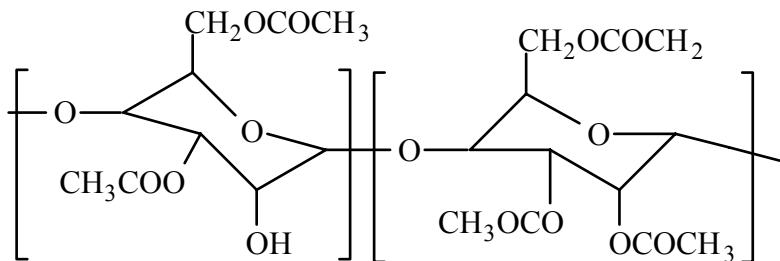
PI 1 = aromatic polyimide:

(Haraya et al., *Maku*, **11**(1), 48-52 (1986))



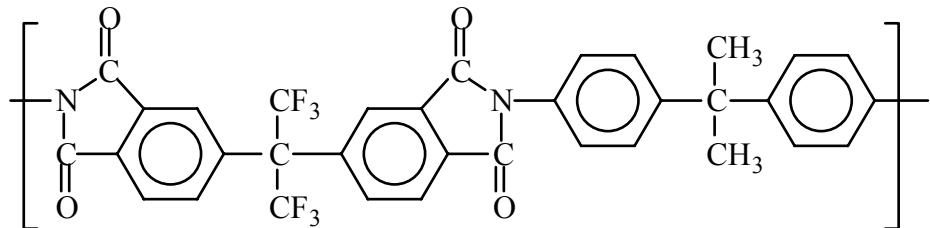
CA = Cellulose Acetate (DS=2.84)

(Puleo et al., *J. Membr. Sci.*, **47**, 301-332 (1989))

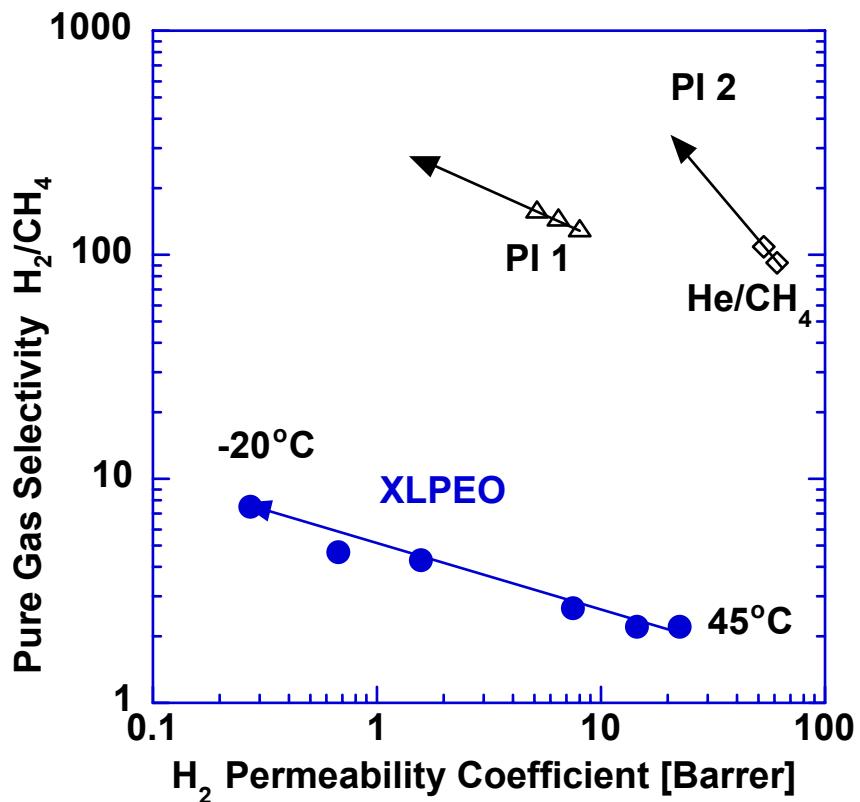


PI 2 = aromatic polyimide (6FDA-IPDA):

(Kim & Koros, *J. Membr. Sci.*, **46**, 43-56 (1989))



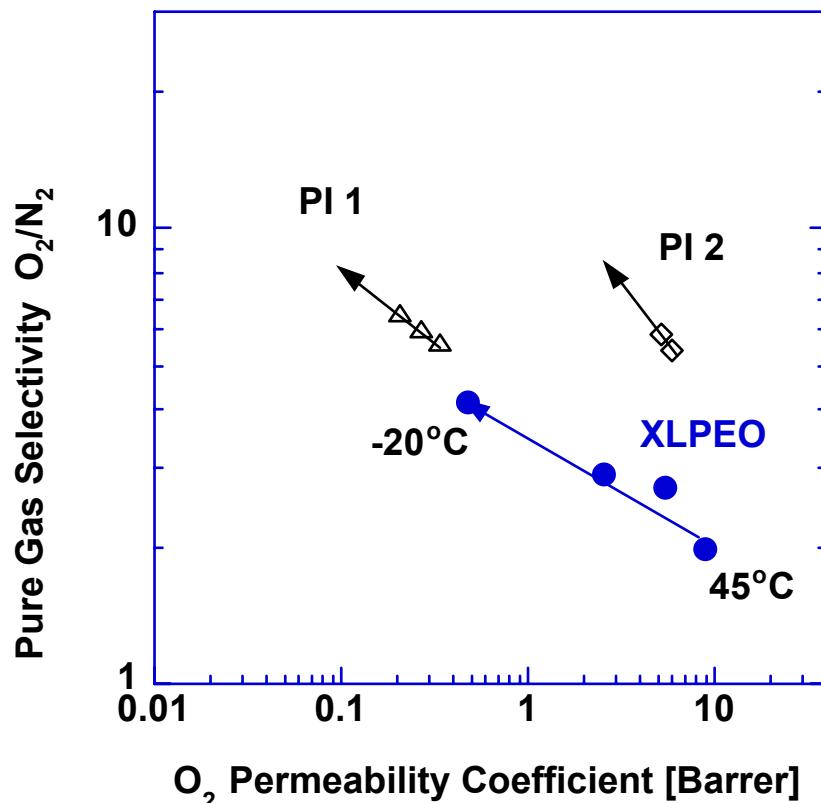
H_2/CH_4 and O_2/N_2 Separation



$$\frac{D_{\text{H}_2}}{D_{\text{CH}_4}} \gg 1$$

$$\frac{S_{\text{H}_2}}{S_{\text{CH}_4}} < 1$$

$$\Delta d = -0.91 \text{\AA}; \Delta T_c = -157.81 \text{K}$$

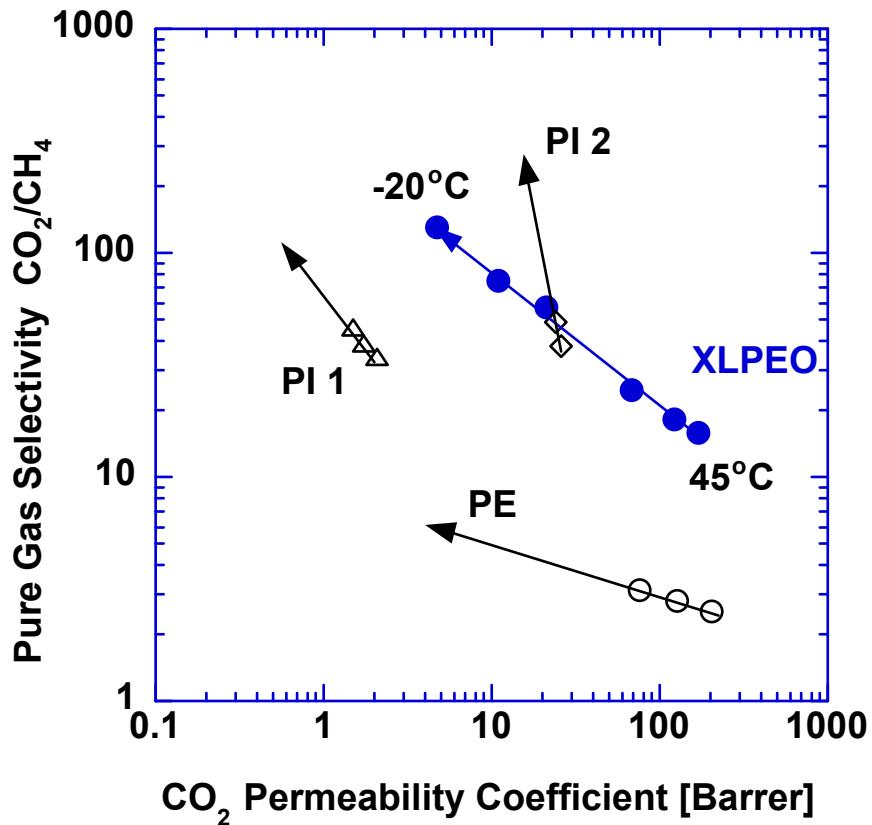


$$\frac{D_{\text{O}_2}}{D_{\text{N}_2}} > 1$$

$$\frac{S_{\text{O}_2}}{S_{\text{N}_2}} > 1$$

$$\Delta d = -0.18 \text{\AA}; \Delta T_c = 28.4 \text{K}$$

CO_2/CH_4 and CO_2/N_2 Separation

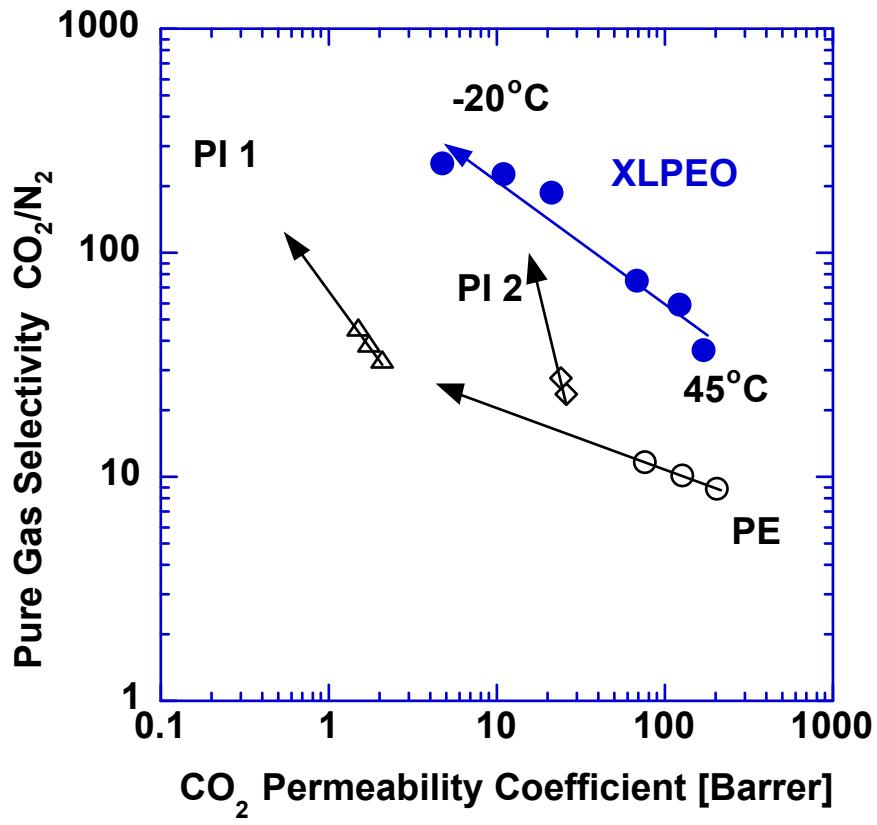


$$\frac{D_{\text{CO}_2}}{D_{\text{CH}_4}} > 1$$

$$\frac{S_{\text{CO}_2}}{S_{\text{CH}_4}} > 1$$

$$\Delta d = -0.5 \text{\AA};$$

$$\Delta T_c = 113.16 \text{K}$$



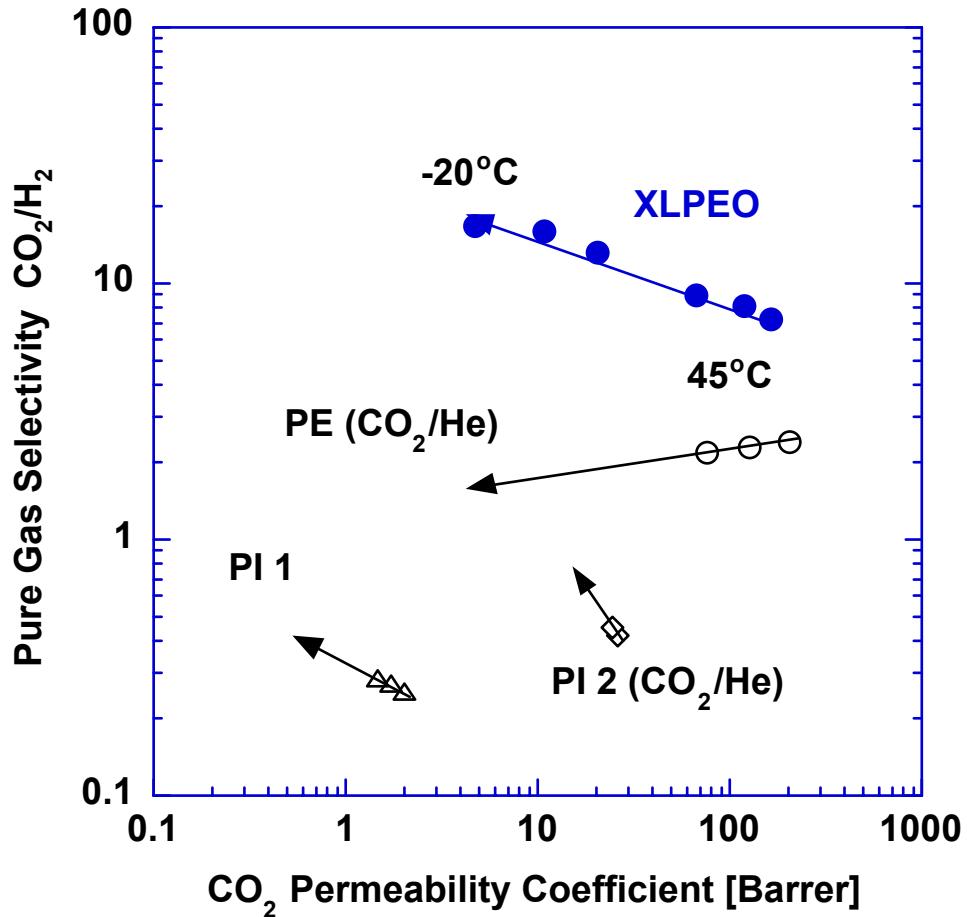
$$\frac{D_{\text{CO}_2}}{D_{\text{N}_2}} > 1$$

$$\frac{S_{\text{CO}_2}}{S_{\text{N}_2}} > 1$$

$$\Delta d = -0.34 \text{\AA};$$

$$\Delta T_c = 178.01 \text{K}$$

CO_2/H_2 Separation



$$\frac{D_{\text{CO}_2}}{D_{\text{H}_2}} \ll 1$$

$$\frac{S_{\text{CO}_2}}{S_{\text{H}_2}} \gg 1$$

$$\Delta d = 0.41 \text{\AA};$$

$$\Delta T_c = 271 \text{K}$$

Summary

- Nanoparticles can be used to alter polymer chain packing and interactions with penetrants to alter transport properties.
- New theory/models needed to predict effect of nanoparticles on transport properties.
- Crosslinked poly(ethylene oxide) is an interesting matrix polymer for CO₂/H₂ separation.
- Temperature might be manipulated to achieve better separation performance.